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<p>(21) International Application Number: PCT/GB98/00618</p> <p>(22) International Filing Date: 26 February 1998 (26.02.98)</p> <p>(30) Priority Data: 9705149.4 13 March 1997 (13.03.97) GB</p> <p>(71) Applicant (for all designated States except US): EA TECHNOLOGY LIMITED [GB/GB]; Capenhurst, Chester CH1 6ES (GB).</p> <p>(72) Inventor; and (75) Inventor/Applicant (for US only): GILROY, Daniel [GB/GB]; 56 Hallfields Road, Tarvin, Chester CH3 8ET (GB).</p> <p>(74) Agent: BOULT WADE TENNANT; 27 Fumival Street, London EC4A 1PQ (GB).</p>		<p>(81) Designated States: AU, CA, JP, NZ, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: A METHOD FOR CHROMATING METALS HAVING SURFACE OXIDE LAYERS</p> <p>(57) Abstract</p> <p>A method for chromating the surface of metals having surface oxide layers which comprises immersing the metal surface or surfaces to be chromated in a neutral or alkaline solution containing trivalent chromium ions and applying a series of pulses of electrical current between the metal surface acting as a cathode and an anode both located in the solution.</p>		

A METHOD FOR CHROMATING METALS
HAVING SURFACE OXIDE LAYERS

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Background of the Invention

Field of the Invention

10 This invention relates to a method of surface-treatment of metals which is known as Conversion Coating or Chromating.

Description of the Prior Art

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The strongly oxidising properties of hexavalent chromium - Cr(VI) - are utilised in the surface treatment known as Conversion Coating or Chromating. The metallic objects to be processed are normally immersed in appropriate solutions, to produce coatings which increase the resistance to corrosion, and improve the adherence of any subsequently applied organic layer, paint or lacquer. Occasionally the procedure may be combined with additional electrochemical steps. Unfortunately, the usage of the chromium(VI) containing chemicals has associated risks, for example, the materials are carcinogenic, and are a fire hazard. Disposal of the spent solutions is also costly, since reduction to the tri-valent state, which is non-toxic, is generally required. Hence, there is a need for viable alternative treatments.

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An important aspect of the use of conversion coatings is that they should provide enhanced protection

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against corrosion, and the inventor of the present patent application, in collaboration with others, has developed rapid electrochemical tests for assessing this property. ("Metal Finishing" Vol. 94, No. 4, pages 26-30). These test methods were shown to give results comparable to the often used salt spray tests. In the present application one particular method has been used extensively. This is referred to as the multi-sweep test with charge integration (MSCI test). Multiple potential scans at slow speeds of $2-10 \text{ mV s}^{-1}$ are applied from the open circuit potential to anodic potentials above the pitting region, and back again, in mixed sulphate/chloride media. The currents are integrated and plotted as a function of sweep number. High values of charge are indicative of pitting in a given cycle. The behaviour is found to depend on surface treatment. Examples of the results obtained are given in Figure 1. Here the effect of replacing hexavalent chromium ions with trivalent chromium ions in a standard chromating bath is shown. The Figure plots charge passed per cycle during potentiodynamic sweeps as a function of scan number. The voltage limits were -0.8 V and 0.35 V in $0.1 \text{ M Na}_2\text{SO}_4 + 0.01 \text{ M NaCl}$ solution. The samples were chromated in nitrate based baths. The Cr(VI) contents of the baths and the immersion times were 100%, 180 s (No.1), 75%, 180 s (No.2), 50%, 900 s (No.3), 25%, 1800 s (No.4), and 0%, 1800 s (No.5), Sample No. 6 was not chromated. It will be seen that only with 100% or 75% of the chromium ions as Cr(VI) does the integrated charge remain low on each potential cycle. In the other cases higher charges indicate that depassivation phenomena have occurred.

Representative examples of chromating baths, free of

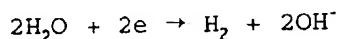
hexavalent chromium, as published in the literature, were examined. The solutions were prepared, the samples were treated according to the recommended procedures, and the samples were tested using the MSCI test. In all cases the results were not as good as those obtained by the normal chromating method using Cr(VI), and usually the results were similar to those for the untreated metal. In summary, therefore, the alternative treatments give less protection against corrosion than the standard chromating technique using Cr(VI).

It has been shown that the films formed on aluminium during the normal chromating procedure using Cr(VI) ions, that is with solutions made from chromium trioxide and dichromate together with other additives, consist of mixtures of aluminium and chromium oxides, namely Al_2O_3 and Cr_2O_3 (J.K. Hawkins *et al.*, Corrosion Science Vol. 27, No. 4, pages 391-399 (1987); and G.M. Brown *et al.*, Corrosion Science Vol. 33 No. 9, pages 1371-1385 (1992)). This implies that the hexavalent ions present in the solution are reduced to the trivalent state.

To complete the discussion of the prior art, it has been known in the field of electrochemical metal-plating to deposit chromium metal from a buffered acidic solution containing trivalent chromium ions, by direct reduction of the metal ions. Such electro-metal plating should not be confused with chromating, i.e. the application of an oxide conversion coating to a metal surface.

Summary of the Invention

It has been realised that an alternative approach to chromating would be to start with trivalent ions in the solution and to precipitate the oxide Cr_2O_3 on the metal surface by making the conditions adjacent to the metal alkaline. In the present invention this is achieved by applying cathodic electrical current pulses to the metal. The passage of current liberates hydrogen according to the equation:



and hydroxide ions are formed in the solution. After an oxide has precipitated the current is switched off and the solution allowed to relax so that chromium ions may be replenished near the interface. The process can then be repeated many times in order that an adherent layer may be built up.

Thus, in accord with the present invention there is provided a method for chromating the surface of metals having surface oxide layers which comprises immersing the metal surface or surfaces to be chromated in a neutral or alkaline solution containing trivalent chromium ions and applying a series of pulses of electrical current between the metal surface acting as a cathode and an anode both located in the solution.

The most suitable composition for the Cr(III) solution the optimum magnitude and duration of the current pulse, and the delay time when the current is off may readily be determined by experiments as shown below.

It will be seen that the method eliminates the use of

toxic hexavalent chromium compounds.

Example

5 Best results were obtained from solutions of 0.02M chromium potassium sulphate, with sodium sulphate (0.1M) added to increase the conductivity (pH 3.8). Initially, cathodic pulses of 1 mA cm⁻² were applied, in line with those suggested by chromium uptake
10 measurements during chromating. However, higher currents gave better results. Typical pulse sequences are shown in the following Table.

15	Current (mA cm ⁻²)	Cathodic time (s)	Off time (s)	Anodic time (s)	Off time (s)	Cycles
	100	0.1	3	--	--	100
	100	--	--	0.1	3	100
	10	0.1	3	--	--	100
	100	0.05	3	--	--	100
20	100	0.025	3	--	--	400
	100	0.05	3	--	--	200
	100	0.1	3	0.1	3	100*
	200	0.1	3	--	--	500
	10	0.1	3	--	--	1000

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* 2 Cathodic pulses + o.c., then 1 Anodic pulse + o.c., repeated 100 times.
(o.c. = open circuit, i.e. current switched off)

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Using these techniques, a green film was formed on 36 cm² of an aluminium plate by cathodic pulsing at 10 mA cm⁻² (0.1 s on, 3 s off, 600 cycles). The cathodic transients measured during the running of this

sequence indicated that the specimen potential became more negative as the film built up, because of the increasing resistance of the formed layer.

5 Specimens were then tested by the usual MSCI method, the results being shown in Figure 2, which illustrates cyclic voltammetry with a charge integration test in a sulphate/chloride medium. The specimens had previously been pulse polarised in a chromium
10 potassium sulphate solution, with and without added sulphate (continuous and dashed lines respectively) for 600 cycles. The plot for untreated aluminium is also shown (dotted line). The integrated charges are low, showing that protection has been enhanced, and no
15 pitting phenomena were observed during the test transients. The magnitudes of the integrated charges are comparable to those of conventionally chromated specimens. An untreated aluminium specimen shows high charges in the initial cycles, indicative of pitting.

20 Measurements of the chromium uptake of the surface gave values of $123 \mu\text{g cm}^{-2}$ for 666 cycles (10 mA cm^{-2} , 0.1 s) in sulphate free solution, and $91 \mu\text{g cm}^{-2}$ for 555 cycles in the solution with added sulphate. Some
25 degree of control of the film thickness is therefore available. The quoted values are higher than those on aluminium treated in a standard chromating medium.

CLAIMS

1. A method for chromating the surface of metals having surface oxide layers which comprises immersing the metal surface or surfaces to be chromated in a neutral or alkaline solution containing trivalent chromium ions and applying a series of pulses of electrical current between the metal surface acting as a cathode and an anode both located in the solution.
2. A method as claimed in claim 1 wherein the metal is aluminium.
3. A method as claimed in claim 1 or claim 2 in which the conductivity of the solution is increased by the inclusion of sodium sulphate in the solution.
4. A method as claimed in any one of the preceding claims in which the applied current density is between 1 and 200 mA cm⁻², and preferably between 10 and 100 mA cm⁻², the pulse lengths are between 0.01 and 1 s, and preferably between 0.01 and 0.1 s, and the delay between pulses is between 0.5 and 10 s and preferably between 0.5 and 3 s.
5. A method as claimed in any of the preceding claims in which the number of pulses applied is between 100 and 1000.
6. A method as claimed in any one of the preceding claims wherein the thickness of the deposited layer is controlled by the number of pulses applied.
7. A method as claimed in any one of claims 1 and 3 to 6 wherein the metal is selected from magnesium and

its alloys, copper and its alloys, nickel, silver, tin and its alloys, aluminium alloys, chromium and chromium coatings, steel, titanium and its alloys, and zirconium.

FIG. 1

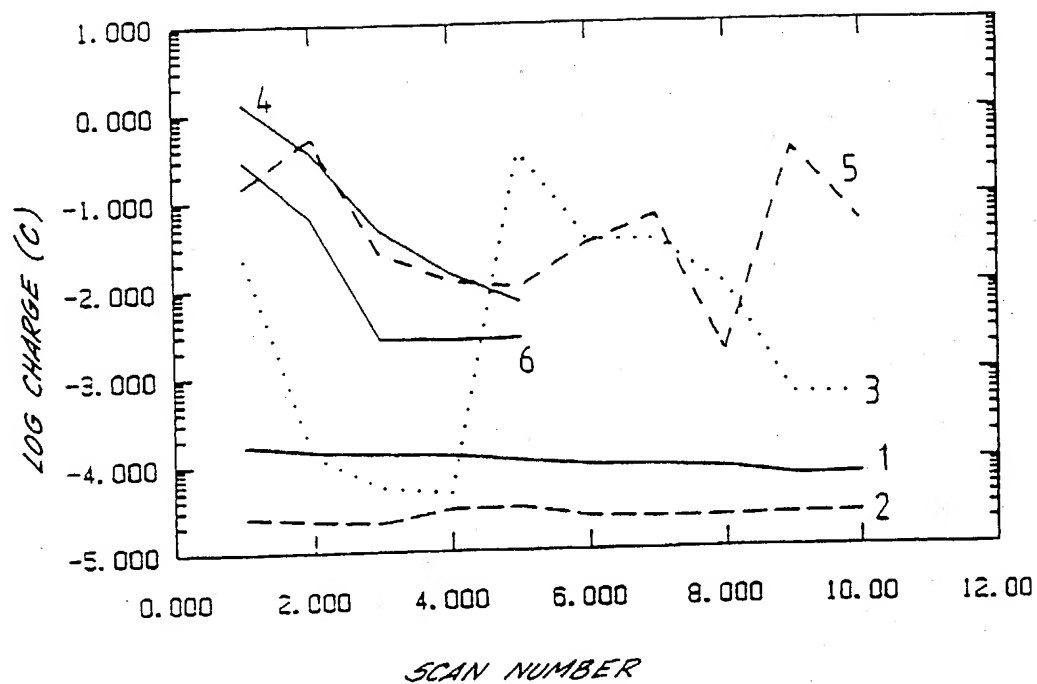
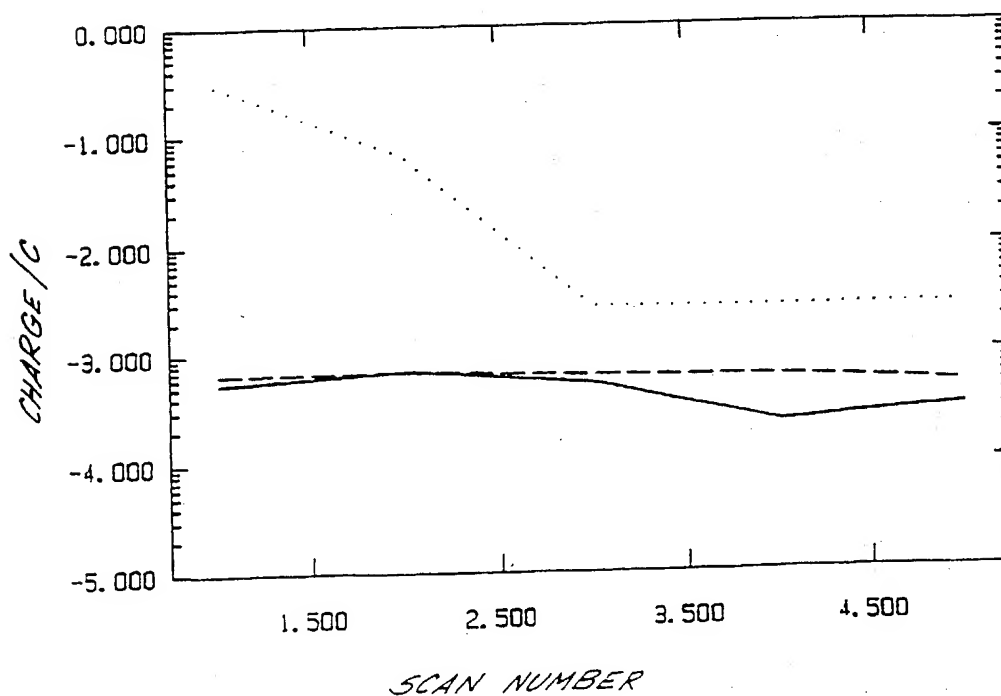


FIG. 2



INTERNATIONAL SEARCH REPORT

Int. Application No
PCT/GB 98/00613

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C25D11/38 C25D5/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C25D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
A	GB 2 204 594 A (SVILUPPO MATERIALI SPA) 16 November 1988 ---	
A	EP 0 747 510 A (ATOTECH USA INC) 11 December 1996 ---	
A	ZHENMI TU ET AL: "PULSE PLATING WITH A TRIVALENT CHROMIUM PLATING BATH" PLATING AND SURFACE FINISHING, vol. 77, no. 10, 1 October 1990, pages 55-57, XP000201505 -----	

☐ Further documents are listed in the continuation of box C

☒ Patent family members are listed in annex

Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

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- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "3" document member of the same patent family

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040. Tx 31 651 epo nl.
Fax (+31-70) 340-3016

Authorized officer

Van Leeuwen, R

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 98/00618

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